On the heavy-fermion behavior of the pyrochlore transition-metal oxide LiV_2O_4

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Motivated by the heavy fermion Fermi liquid (HFFL) features observed at low-T in the pyrochlore LiV_2O_4, we consider a material-specific model that includes aspects of the local quantum chemistry, the geometrically frustrated lattice structure, and strong correlations in a *single* approach. In particular, we show how geometrical frustration (GF) gives rise to a crossover scale, $T^* << J$, the intersite (AF) exchange, below which the metallic system shows HFFL features. Our scenario is a specific realization of the importance of GF effects in driving HFFL behavior in LiV_2O_4, and provides a natural understanding of various puzzling features observed experimentally.

Systems of the type AB_2O_4 with a magnetic B site consistently show strange properties. In particular, systems with $B = Ti, V, Cr$ are interesting because the d electrons occupy t_{2g} orbitals that do *not* hybridize with the oxygen orbitals along certain directions [1–5]. In the geometrically frustrated structure, the nearest neighbor exchange interaction dominates with a maximization of frustration. Concomitantly, only 3d bands (t_{2g}) cross the Fermi level (μ), leading one to have to deal with the ubiquitous strong correlations. With a divalent A-ion, the B site has integral valence, giving rise to Mott insulating behavior with frustrated magnetism, e. g., in ZnV_2O_4. On the other hand, with a monovalent A site, B is mixed-valent, resulting in a narrow-band metal. This combination of frustrated magnetism and correlated metallic behavior leads to a range of complex and unusual manifestations, from superconductivity, for example in $LiTi_2O_4$, via heavy-fermion Fermi liquid (HFFL) behavior in LiV_2O_4, to spin-glass behavior in other systems.

The best example in the second category above is LiV_2O_4 [6], a paramagnetic metal for $T > 0.01K$. The low-T Sommerfeld constant achieves its highest value for a d-electron system, $0.42J/mole/K^2$ at $T = 1.5K$. The resistivity, the Woods-Saxon ratio, as well as the Wilson ratio all exhibit behaviors expected for prototypical rare-earth based HFFL metals [6]. Importance of geometrical frustration (GF) for magnetic properties is shown by the absence of a low-T magnetic instability, and further vindicated by neutron scattering (INS) studies [7], which reveal a response characteristic of *insulating*, frustrated magnets. This leads one to ask: What is the role of GF in driving HFFL behavior? More precisely, how does one reconcile the HFFL behavior in thermodynamics and transport with a magnetic response characteristic of frustrated, *insulating* magnets? What is the role of strong correlations in the 3d bands? How do these two subsystems couple to (affect) each other at low-T?

Much attention has been devoted to these issues. LDA bandstructure calculations indeed show that the 3d t_{2g} bands alone cross the Fermi level [8]. A trigonal distortion splits the three-fold degenerate t_{2g} states into the (lower lying) singlet A_{1g} with a bandwidth of $1eV$, and an E_g doublet with a bandwidth of $2eV$ in the solid. Given the formal $d^{1.5}$ state of V, the A_{1g} band is half-filled, and the E_g bands are quarter-filled, leading [9] to suggestions that an effective Anderson model could be used. However, approaches along these lines require the rather ad-hoc introduction of a large intersite Kondo coupling to counterbalance the strong local Hund's rule coupling, the origin of which is unclear. Moreover, frustration effects are not important in these pictures. On the other side, Fulde *et al.* [10] have proposed that the V lattice of corner-sharing tetrahedra frustrates charge ordering and leads instead to isolated finite chains of $S = 1/2$ and $S = 1$. The gapless fermionic spin excitations of the $S = 1/2$ chains give the large γ coefficient of the low-T specific heat. This picture needs to be extended to derive the HFFL properties, and to make a detailed comparison with INS results. Varma [11] seeks to understand the HFFL properties by analyzing the energetics of the crossover which a $S \neq 1/2$ impurity must undergo in the Kondo effect. Frustration does not play any role here either. Recently, Burdin *et al.* [12] have studied the role of frustration effects in driving HFFL behavior. However, frustration effects are put in by hand, limiting a direct comparison with the actual material. Lacroix [13] has recently sketched the outlines of a picture for HFFL behavior in d-band oxides with geometrical frustration.

Here, we study a theoretical model that is material-specific and includes *all* the relevant degrees of freedom and explicitly address the questions above. In particular, we show how the HFFL properties are reconciled with the magnetic response characteristic of frustrated, insulating magnets. The choice of the model Hamiltonian is motivated by experimental constraints [6] as well as by results of first-principles LDA calculations [8]:

$$H = H_s + H_b + H_{sb} , \qquad (1)$$

where $H_s = \sum_{ij} J_{ij}\mathbf{S}_i.\mathbf{S}_j$ is the Heisenberg-like $S = 1/2$ Hamiltonian describing the localized spin degrees of freedom originating from the half-filled narrow singlet A_{1g}

band. In LiV_2O_4, the next-nearest neighbor coupling may be important, though its magnitude is not reliably known.

$$H_b = -\sum_{<ij>} t_{ab}(c^\dagger_{ia\sigma}c_{jb\sigma} + h.c) + U\sum_{ia} n_{ia\uparrow}n_{ia\downarrow}$$
$$+ U_{ab}\sum_{i,a,b} n_{ia}n_{ib} \qquad (2)$$

describes the electronic degrees of freedom for the E_g bands. And $H_{sb} = -J_H \sum_{i,a,b} \mathbf{S}_i.(\sigma_{ia} + \sigma_{ib})$ describes the coupling of these two subsystems via a local Hund's rule interaction.

In what follows, H is defined on the fully-frustrated pyrochlore (FFL) lattice, entailing explicit consideration of geometrical frustration effects. To proceed in this complicated situation, and motivated by observations, we make the plausible assumption: The underlying A_{1g} spin configuration does affect the charge dynamics in the E_g band, but that there is no qualitative change in the localized magnetic response coming from the feedback effects due to this carrier dynamics. This assumption is justified later. With this, we follow the following strategy: (i) Treat the spin correlations in the Heisenberg like model on the FFL within a cluster approach capable of correctly treating the short-range fluctuations which drive the spin liquid behavior as observed in INS experiments. (ii) Use the fact that the A_{1g} spins are coupled to the correlated electrons in the E_g band(s), and modify the hopping, t_{ab}, to solve the modified electronic model within the $d = \infty$ approximation, which is the best technique to reliably access dynamical effects of strong, local correlations [14]. As with the A_{1g} spins, the E_g electrons live on the FFL, a fact that is indeed important for a consistent understanding, as we show below.

On the FFL, the electronic dispersion relation (or the spin-wave dispersion for localized spins) has four branches corresponding to the four-sublattice structure inherent in this geometry; two branches are completely flat over the whole Brillouin zone, while the other two form dispersive bands in the solid. Mathematically, $\epsilon_\alpha(\mathbf{k}) = 2t$ for $\alpha = 1, 2$ and, $\epsilon_\alpha(\mathbf{k}) = -2t(1 \pm \sqrt{c_xc_y + c_yc_z + c_zc_x})$ for $\alpha = 3, 4$ $[c_a \equiv cos(k_a/2)]$. Notice that the free dispersion alone gives a two-band structure in the unperturbed DOS (see Fig. 2, with $U_{ab} = 0$). For the A_{1g} spins, one replaces $\epsilon(\mathbf{k})$ by $J(\mathbf{q})$ and t by J in the above equations. From the susceptibility data [6], a large $g = 2.23$ is inferred, suggesting strong *ferromagnetic* coupling between the carriers in the E_g band and the "localized" spins in the A_{1g} band (large J_H). So the carrier hopping rate is strongly coupled to, and reflects the underlying (A_{1g}) spin correlations: $t_{ab}(\mathbf{S}) \to t_{ab}\sqrt{1+ < \mathbf{S}_i.\mathbf{S}_j > /2S^2}$ [15].

As mentioned before, we first focus on the A_{1g} correlations, assuming, in accordance with LDA calculations, that this narrow band is completely occupied by one localized electron per site. Following [16], we employ a self-consistently embedded cluster approach that treats the spin correlations in one tetrahedron *exactly* and mimics the influence of the remaining tetrahedra by inhomogeneous, selfconsistently determined magnetic fields. The resulting static spin susceptibility is shown in Fig. 1. $\chi_s(T)$ shows a Curie-Weiss (CW)-like form at high-T, followed by a maximum at lower $T^* << J$. And $\chi(\mathbf{q}, T) = g(\mathbf{q})\chi(T)$, consistent with [17]. At very low T, a gap opens up in the spin excitation spectrum; by fitting $\chi(\mathbf{q}, T)$ to an exponential form, we extract the spin correlation length, which turns out to be weakly T-dependent and never exceeds a lattice spacing, in qualitative agreement with [17]. The resulting physical picture is that of a strongly fluctuating spin system, with extreme short-range AF correlations and *no* long-range order down to $T = 0$. This agrees with the absence of magnetic order found experimentally, as also with the fact that the CW constant corresponds to $S = 1/2$, and that $\Theta_{CW} < 0$.
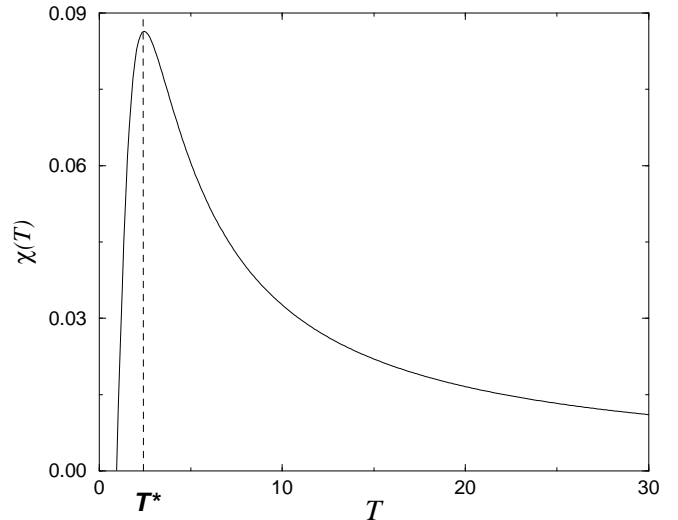

FIG. 1. Magnetic susceptibility of the localized spins in the A_{1g} band of the pyrochlore lattice obtained from a self-consistent embedded cluster approach [14]. $T^\star$ marks the crossover temperature below which the system exhibits HFFL behavior.

A potentially interesting situation now occurs: the carrier hopping, as mentioned above, reflects the A_{1g} spin correlations as well as intrinsic geometric frustration effects from the FFL structure, preventing the tendency to charge- and/or orbital ordering (COO). This explicitly realizes the mechanism for suppression of COO proposed by Fulde *et al.* [10]; however, in our approach, it does not lead to formation of $S = 1/2$ and $S = 1$ rings and chains. The difference from the CMR manganites [11] also has a consistent explanation within this picture: the frustrated kinetic energy selfconsistently prevents the possibility for the A_{1g} spins to align (via "double exchange") ferromagnetically, in contrast to what happens in manganites [15].

Next, consider the E_g-band electrons strongly coupled to the A_{1g} spins via a local (ferromagnetic) Hund's rule coupling:

$$H_{el} = -t \sum_{<ij>,\sigma} (c^\dagger_{ia\sigma} c_{jb\sigma} + h.c.) + U \sum_{i,a} n_{ia\uparrow} n_{ia\downarrow}$$
$$+ U_{ab} \sum_i n_{ia} n_{ib} - J_H \sum_i \mathbf{S}_i.(\sigma_{ia} + \sigma_{ib}) , \quad (3)$$

where a and b refer to the doubly degenerate E_g states in the t_{2g} sector, defined on the FFL. With the strong J_H, the "double exchange" projection transforms the problem to that of spinless fermions, but the hopping is modulated by the underlying, frustrated spin correlations in the A_{1g} band. The Hamiltonian is,

$$H_{el} = - \sum_{<ij>,a,b} t_{ij}(\mathbf{S})(c^\dagger_{ia} c_{jb} + h.c) + U_{ab} \sum_i n_{ia} n_{ib} ,$$
$$(4)$$

where we set $U, J_H \to \infty$. Relabelling $c_a = c_\uparrow$ and $c_b = c_\downarrow$, we are left with a Hubbard-like model with a non-trivial hopping term:

$$H_{el} = - \sum_{<ij>,\sigma} t^\sigma_{ij}(\mathbf{S})(c^\dagger_{i\sigma} c_{j\sigma} + h.c) + U_{ab} \sum_i n_{i\uparrow} n_{i\downarrow} . \quad (5)$$

We use the $d = \infty$ approximation to solve the Hubbard-like model on the FFL. This interesting problem has non-trivial solution(s), related to the one-electron dispersion on the FFL. In particular, close to $n = 1$, non-Fermi liquid behavior is expected due to the strong scattering off the completely flat bands. Fortunately, for LiV_2O_4, one deals with an almost quarter-filled band, rendering the flat-band singularities irrelevant. The above electronic model is now solved using the iterated perturbation theory (IPT) at slightly less than quarter-filling and at finite T [18].

Fig. 2 shows the evolution of the one-electron local spectral function, $\rho(\omega)$. As U_{ab} increases, a sharp collective Kondo-like peak appears and gets narrower around μ. The appearance of upper and lower "Hubbard" bands (these appear as shoulder-like features in the range $-2 \leq \omega \leq 2$ in Fig.2), reflecting suppression of charge fluctuations near quarter-filling, is also clear. Formation of heavy quasiparticles is reflected in the quasiparticle renormalization constant, $Z(\mu)$, defined as $Z(\mu) = \left[1 - \frac{d\Sigma'(\omega)}{d\omega}|_{\omega=\mu}\right]^{-1}$.

$Z(\mu)$ decreases monotonically with increasing U_{ab}. That this correlated metallic state with heavy fermion mass $(m^*/m = 1/Z(\mu))$ is a FL is clear from the fact that $\text{Im}\Sigma(\omega \simeq \mu) = -b(\omega - \mu)^2$. Importance of the filling is shown by the fact that charge fluctuations are enhanced, while spin fluctuations diminish in importance as n is decreased further (not shown). Our results are in complete agreement with those of Imai *et al.* [19] for a

two-orbital Hubbard model with finite U and J_H, and the HFFL behavior in our model should persist when large, finite U and J_H are included. The computed integrated photoemission lineshape in the HFFL phase is shown in Fig. 3. Signatures of strong electronic correlations in the E_g band are visible as shake-up features: a broad, incoherent, lower Hubbard band feature well separated from the narrow quasiparticle resonance. This should provide evidence in favor of our modelling of the E_g manifold.
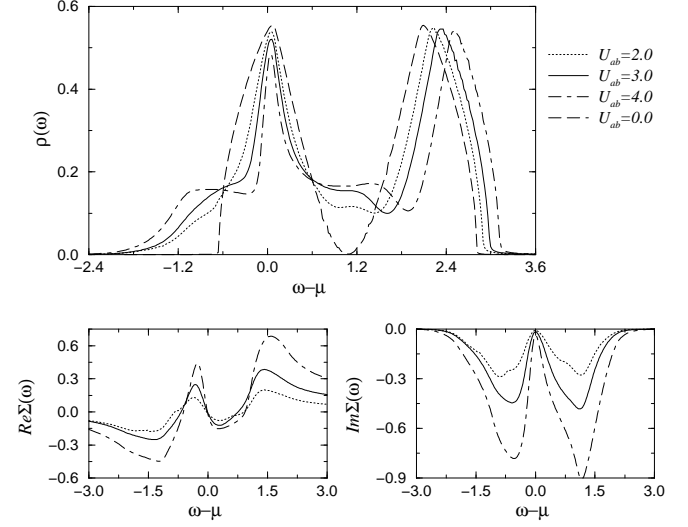

FIG. 2. Local spectral density (a), and real (b) and imaginary (c) parts of the s.p. self-energy for the Hubbard model on the fully-frustated pyrochlore lattice for diffetent values of the Coulomb interaction in the E_g sector.
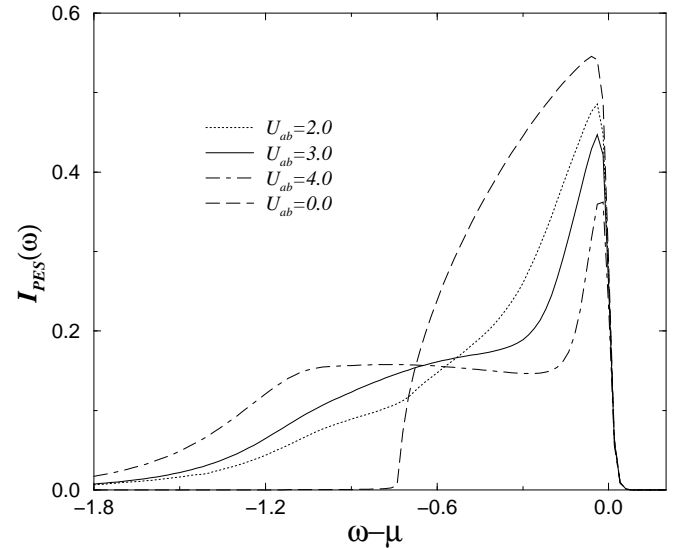

FIG. 3. Integrated photoemission lineshapes of the Hubbard model on the fully-frustrated pyrochlore lattice for different values of U_{ab}.

Finally, consider the question of selfconsistency due to the coupling of the correlated carriers to the A_{1g} spin

fluctuations. At low $T < T^*$, the dynamical spin susceptibility behaves like $\chi"(\Omega) \simeq (\Omega/T^*)$ in the HFFL regime (see below). The leading-order correction to the self-energy of the correlated carriers is $\Sigma(i\omega_n) = (J_H^2/\beta)\sum_m \chi(i\Omega_m)G(i\omega_n - i\Omega_m)$. In the HFFL regime, $G(\tau) \simeq (1/\tau)$ for long times, and $\Sigma(\omega)$ remains qualitatively unchanged from its FL-like form (see above) as long as $\chi"(\Omega) \simeq \Omega/T^*$. This analysis ceases its validity above T^*, where the susceptibility gets increasingly dominated by fluctuating local moment contributions. Inserting the resulting $\Sigma(\omega)$ into the calculation for the susceptibility (notice that at low T, the spin susceptibility of the localized spins is gapped) leads again to the Ω/T^* form, apart from prefactors. Thus, at low $T < T^*$, selfconsistency leads only to a minor quantitative modification of our results.

Let us discuss the implications of our calculation. Since the magnetic correlation length is T-independent below $T^* << J$ (corresponding to the point at which $\chi(T)$ shows a peak, see Fig. 1) this sets the scale below which the hopping, t, can be treated as constant in H_b. Above T^*, the influence of the A_{1g} spin correlations drive the system into a local-moment metallic regime, but below this scale, HFFL-like quasiparticles develop as shown above. We thus identify the low-T crossover scale seen in experiments with the T-dependence of the frustrated spin dynamics in the A_{1g} sector coupled to correlated E_g carriers. This implies that the mechanism for HFFL behavior in our scenario is intimately linked to the local-moment magnetism of the FFL, and is drastically different from the conventional view, where a band of uncorrelated [20] carriers collectively screens localized moments at every site. Our calculation explicitly realizes the suggestions of Lacroix [13], but goes much further, showing clearly how short-ranged, spin-liquid-like local moment correlations in the A_{1g} sector on the FFL are related to the onset of HFFL behavior. In our opinion, a mean-field-like decoupling *cannot* describe the crossover at T^* adequately, since the spin liquid behavior is driven precisely by strong fluctuations beyond the mean-field picture.

Given the HFFL metallic state below T^*, the electronic specific heat, behaves like $\mathcal{C}_{el}(T) \simeq (T/T^*)$, with a peak at T^*. The local dynamical spin susceptibility $J\chi"(\omega) \simeq (\omega/T^*)$, so the NMR relaxation rate is Korringa like, $1/T_1 \simeq (T/JT^*)$. The uniform spin susceptibility $\chi \simeq O(1/J)$ at low T. The calculation of the resistivity does not involve vertex corrections within DMFT. At low T, in the HFFL phase, we obtain $\rho_{dc}(T) \simeq (T/T^*)^2$, implying that the Kadowaki-Woods relation is obeyed, as in conventional heavy fermions. The Wilson ratio $W = T\chi/C_{el} \simeq O(T^*/J)$, again as in the traditional case. All these results are indeed consistent with thermodynamic, transport and magnetic measurements performed on LiV_2O_4.

A detailed calculation of the dynamical spin response of the FFL is a fascinating problem in itself, and is inti-mately linked to the details of the T-dependence of various quantities as T crosses T^*. We plan to address this more detailed issue in a longer separate work.

To conclude, a theoretical understanding of the various physical features of the frustrated, 3d, heavy fermion metal, LiV_2O_4 is proposed. In particular, we have shown how the HFFL thermodynamics and transport [6] can be reconciled with a magnetic response characteristic of frustrated, insulating magnets [7] and how the experimentally observed crossover scale (T^*) is directly related to the T dependence of the frustrated spin dynamics in the A_{1g} sector. To our knowledge, this is the first attempt that explicitly includes specific lattice structure, magnetic frustration and strong correlation effects within a single picture. Our picture is radically different from conventional ones, and is a concrete realization of the importance of geometrical frustration effects in driving HFFL behavior in LiV_2O_4.

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